

Screening of Magnetic Moment at Co Impurity in Cu Host

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Cobalt impurity located in the bulk copper is described making use of the multi-orbital Anderson impurity model that is parametrized to match the electronic structure from the local density approximation, and solved using the Lanczos method. We concentrate on the many-body description of the ground state and excitation spectra. The calculations yield a nonmagnetic ground state for the impurity atom. The computed spectral densities are in a good agreement with those obtained using the quantum Monte Carlo method.

INTRODUCTION

The Kondo effect, known for nearly 80 years, is one of the first discovered correlation phenomena in solid state physics [1]. It occurs when the magnetic elements with partially filled d -, or f -orbitals are incorporated into a non-magnetic host metal. The most prominent macroscopic hallmark of the Kondo effect is the resistance minimum at low temperature found for metals with magnetic impurities [1]. At low temperature, the impurity spin is effectively screened by the conduction electrons. Although the phenomenon is well known for a long time, the theoretical description as well as the experimental investigations are challenging subjects of modern solid state research.

In this work we revisit the electronic and magnetic structure for the Co impurity in Cu. When the conventional local-spin-density approximation (LSDA), the generalized-gradient approximations (GGA) or their Hartree-Fock-type extension (LDA+U) are used, they produce broken symmetry solutions with non-zero spin M_S and orbital M_L moments on the impurity site even without an external magnetic field. The true dynamical solution of an impurity in a non-magnetic host yields $M_S = 0$ and $M_L = 0$ when no external magnetic field is applied. In order to go beyond the static mean-field and to incorporate the dynamical electron correlations, we solve a single impurity Anderson model (SIAM) whose parameters are extracted from LDA calculations using the finite-temperature exact diagonalization (ED) method.

We evaluate the spectral density at the Co impurity in Cu and make a comparison with published quantum Monte Carlo (QMC) results [2]. Finally, we analyse the possibility of forming a singlet ground state which means the dynamical screening of the Co-impurity local moment by the conduction electron bath.

LDA

As a computational model we use a CoCu₁₅ supercell shown in Fig. 1. This supercell is chosen to keep Co and its 12 nearest Cu neighbors separated from other impurity atoms. No relaxation is performed as it is not essential for the close packed *fcc* structure. We use the lattice constant of elemental Cu, $a = 6.82$ a.u.

All calculations are performed making use of a relativistic version (with spin-orbit coupling (SOC)) of LDA implemented in the full-potential linearized augmented plane wave (FP-LAPW) basis [3]. The radii of the atomic muffin-tin (MT) spheres are set to 2.2 a.u. for both Co and Cu. The parameter $R \times K_{\max} = 7.7$ determined the basis set size and the Brillouin zone was sampled with 343 k points. We checked that a finer sampling with 729 k points does not modify the results.

SINGLE IMPURITY ANDERSON MODEL

First we consider the effective SIAM

$$H = \sum_{k\sigma} \epsilon_k b_{k\sigma}^\dagger b_{k\sigma} + \sum_{m\sigma} \epsilon_d d_{m\sigma}^\dagger d_{m\sigma} + \sum_{mk\sigma} (V_{mk} d_{m\sigma}^\dagger b_{k\sigma} + h.c.) + \frac{1}{2} \sum_{\substack{mm'm'' \\ m'''\sigma\sigma'}} U_{mm'm''m'''} d_{m\sigma}^\dagger d_{m'\sigma'}^\dagger d_{m'''\sigma'} d_{m''\sigma}. \quad (1)$$

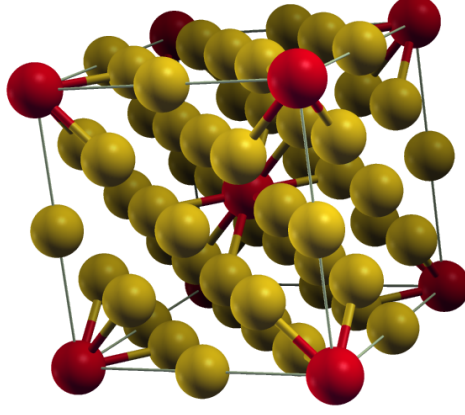


FIG. 1: (Color online) The crystal structure of CoCu_{15} . The red spheres represent the Co atoms whereas the gold represent the Cu atoms.

The operator $d_{m\sigma}^\dagger$ creates an electron in the impurity d shell with energy ϵ_d and $b_{k\sigma}^\dagger$ creates an electron in the conduction bands of the host with corresponding energy ϵ_k . The impurity site is labeled by the magnetic quantum number m and spin $\sigma = \{\uparrow, \downarrow\}$, and the conduction band of the host by a quantum number k and spin σ . The conduction states are dominantly composed of s and p bands of Cu. Their coupling to the impurity orbitals is described by the hybridization parameters V_{mk} . The Coulomb interaction parameters which enter the last term in Eq.(1) are taken as external parameters of the model and their particular choice will be discussed below.

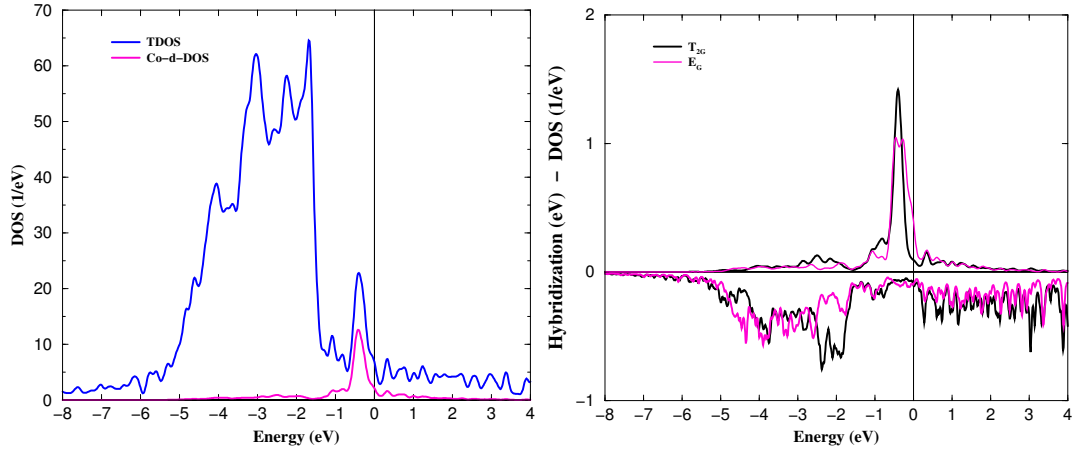


FIG. 2: (Color online) (Left) The total LDA DOS (TDOS) and Co d -orbital LDA DOS (Co-d-DOS) of the Co impurity in Cu bulk, (right) LDA t_{2g} and e_g projected DOS and LDA hybridization function $\frac{1}{\pi}\Delta(\epsilon) = -\frac{1}{\pi}\text{Im Tr}[G^{-1}(\epsilon + i\delta)]$ for t_{2g} and e_g orbitals.

Next, following [4], we re-write this model in terms of the energy-dependent d -only "bath" states $|b(\epsilon, m, \sigma)\rangle = \frac{1}{V_m} \sum_k V_{mk} \delta(\epsilon - \epsilon_k) |k\sigma\rangle$ where, $[V_m(\epsilon)]^2 = \sum_k V_{mk}^2 \delta(\epsilon - \epsilon_k) = -\frac{1}{\pi} \Delta_m(\epsilon)$. The Hamiltonian transforms into:

$$H = \sum_{m\sigma} \int \epsilon n_{m\sigma}^b(\epsilon) d\epsilon + \sum_{m\sigma} \epsilon_d n_{m\sigma}^d + \sum_{m\sigma} \int [V_m(\epsilon) d_{m\sigma}^\dagger b_{m\sigma}(\epsilon) + h.c.] d\epsilon + \frac{1}{2} \sum_{\substack{mm'm'' \\ m'''\sigma\sigma'}} U_{mm'm''m'''} d_{m\sigma}^\dagger d_{m'\sigma'}^\dagger d_{m'''\sigma'} d_{m''\sigma}, \quad (2)$$

where $n_{m\sigma}^b(\epsilon) = b_{m\sigma}^\dagger(\epsilon)b_{m\sigma}(\epsilon)$ and $n_{m\sigma}^d = d_{m\sigma}^\dagger d_{m\sigma}$ are the number operators for the bath and for the d electrons of the impurity, respectively. When the last term in Eq.(2) is omitted, the hybridisation function $\Delta_m(\epsilon) = -\pi[V_m(\epsilon)]^2 = -\text{Im}[G(\epsilon)^{-1}]_m$ can be evaluated from the Green function of the Eq.(2), and we assume that it can be approximated by the LDA result for the Co atom in the Cu host. For the ED method to be applicable, the continuum of the bath states is discretized. Finally, the complete SIAM for the five-orbital d shell subject to the full spherically symmetric Coulomb interaction, spin-orbit coupling and a cubic crystal field can be written as [1]

$$H = \sum_{km\sigma} \epsilon_{km} b_{km\sigma}^\dagger b_{km\sigma} + \sum_{m\sigma} \epsilon_d d_{m\sigma}^\dagger d_{m\sigma} + \sum_{mm'\sigma\sigma'} (\xi \mathbf{l} \cdot \mathbf{s} + \Delta_{\mathbf{CF}})_{mm'}^\sigma{}^{\sigma'} d_{m\sigma}^\dagger d_{m'\sigma'} + \sum_{km\sigma} \left(V_{km} d_{m\sigma}^\dagger b_{km\sigma} + \text{h.c.} \right) + \frac{1}{2} \sum_{\substack{mm'm''m''' \\ m'''\sigma\sigma'}} U_{mm'm''m'''} d_{m\sigma}^\dagger d_{m'\sigma'}^\dagger d_{m'''\sigma'} d_{m''\sigma}. \quad (3)$$

The impurity-level position ϵ_d and the bath energies ϵ_{km} are measured from the chemical potential μ , that was set at values which yield the desired $\langle n_d \rangle$. Parameter ξ specifies the strength of the spin-orbit coupling, whereas $\Delta_{\mathbf{CF}}$ corresponds to the strength of the cubic crystal field acting on the impurity. The cubic crystal field splits the d orbitals of the impurity into triply-degenerate $t_{2g} = \{xy, xz, yz\}$ and doubly-degenerate $e_g = \{x^2 - y^2, z^2\}$ blocks, therefore it is given by the energy differences corresponding to the orbitals $\Delta_{\text{CF}}(t_{2g}) - \Delta_{\text{CF}}(e_g)$. The parameters are determined from LDA calculations as $\xi = 0.076$ eV and $\Delta_{\text{CF}}(t_{2g}) - \Delta_{\text{CF}}(e_g) = 0.10$ eV.

PARAMETRIZATION OF THE IMPURITY MODEL

The Lorenzian-like shape of the LDA density of states (DOS) for Co d -orbitals (see Fig. 2) suggests that it can be associated with the well-known solution of the SIAM Eq.(1) with the constant (energy independent) hybridization function Δ . Since we are interested mainly in the ground state and the low-energy excitations, it seems reasonable to take into account only bath states near the Fermi level E_F , where the main part of the LDA Co d -orbital DOS is located. At first, the diagonal matrix elements of Δ matrix in $\gamma = (xz, yz, xy, x^2 - y^2, 3z^2 - r^2)$ basis were averaged over a region $[-0.5, 0.5]$ eV around E_F , and the $V_\gamma^{k=1}$ were determined as $\sqrt{|\Delta_\gamma|}$. The bath parameters ϵ_γ^k were chosen to reproduce the LDA γ -partial occupations n_d^γ . The values of V_γ^k and ϵ_γ^k parameters are given in Tab. I (bath-A). Note that with this choice of the bath, the effective SIAM is the d -states charge-conserving, and since the n_d^γ are related to the d -wave phase shifts δ_d^γ at E_F ($\delta_d^\gamma(E_F) = \pi n_d^\gamma$), the Friedel sum rule [1] is obeyed.

The Coulomb interaction term potential in the Eq.(3) is given by:

$$U_{mm'm''m'''} = \sum_k a_k(mm'm''m''') F_k, \quad (4)$$

$$a_k(mm'm''m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle lm | Y_{kq} | lm'' \rangle \langle lm' | Y_{kq}^* | lm''' \rangle,$$

where $|lm\rangle$ is a spherical harmonic, and F_k are the Slater integrals. The ballpark values for the Coulomb interaction parameters $U = F_0 = 4$ eV and $J = 0.9$ eV ($F_2 = 7.75$ eV, $F_4 = 4.85$ eV) were used in these calculations.

After the parameters of the discrete impurity model are set, the band Lanczos method [5] is utilized to determine the lowest lying eigenstates of the many-body Hamiltonian and to calculate one-particle Green's function G_{SIAM}^d . The resulting d -orbital spectral function $-\text{Im}(G_{\text{SIAM}}^d)/\pi$ is shown in Fig. 3 for the model bath-A with $\langle n_d \rangle = 7.3$, the inverse temperature $\beta = 500$ eV $^{-1}$ was used in these calculations.

In order to examine the numerical stability of the discrete SIAM with respect to the choice of the bath parameters, we added the extra 10 spinorbitals into the bath at the energy of -2 eV below E_F , as given in Tab. I (bath-A+). The corresponding d -orbital spectral function for the model bath-A+ is shown in Fig. 3. Although the details of the spectral peaks depend somewhat on the particular choice of the bath, the overall structure of the spectrum with peak(s) in the vicinity of the Fermi level is preserved. Also, the number of d -electrons $\langle n_d \rangle = 7.3$ remains the same, if μ is the same. Thus we conclude that additional orbitals away from the region near E_F do not contribute significantly to the low energy spectrum.

Next, we examine the effect of the extra orbitals above the Fermi level. Here, we take an average Δ_γ over a region $[-1, 0]$ eV for the first 10 bath spinorbitals, and over a region $[0, 1]$ for another 10 bath spinorbitals. We make a symmetric choice with respect to the E_F for the ϵ_γ^k parameters, and fit the ϵ_γ^k parameters to reproduce the LDA γ -partial occupations n_d^γ . The values of V_γ^k and ϵ_γ^k parameters for this "bath-B" model are given in Tab. I. The d -orbital spectral function for the model bath-B is shown in Fig. 3. It is seen that an extra (to the bath-model A)

bath site (10 spinorbitals) modifies the spectrum in the vicinity of E_F somewhat stronger than additional bath sites at the energies away from E_F .

TABLE I: Values of d-shell partial occupations n_d , Δ_{CF} (eV) and the bath parameters ϵ_γ^k (eV) and V_γ^k (eV) obtained from LDA .

Co in Cu					
γ	xz	yz	xy	$x^2 - y^2$	$3z^2$
n_d^γ	0.715	0.715	0.715	0.72	0.72
Δ_{CF}	0.04	0.04	0.04	-0.06	-0.06
[5x2] bath orbitals (bath A)					
$\epsilon_\gamma^{k=1}$	-0.025	-0.025	-0.025	-0.190	-0.190
$V_\gamma^{k=1}$	0.385	0.385	0.385	0.330	0.330
2x[5x2] bath orbitals (bath A+)					
$\epsilon_\gamma^{k=1}$	-0.025	-0.025	-0.025	-0.190	-0.190
$V_\gamma^{k=1}$	0.385	0.385	0.385	0.330	0.330
$\epsilon_\gamma^{k=2}$	-2.00	-2.00	-2.00	-2.00	-2.00
$V_\gamma^{k=2}$	0.756	0.756	0.756	0.435	0.435
2x[5x2] bath orbitals (bath B)					
$\epsilon_\gamma^{k=1}$	-0.160	-0.160	-0.160	-0.090	-0.090
$V_\gamma^{k=1}$	0.300	0.300	0.300	0.293	0.293
$\epsilon_\gamma^{k=2}$	0.160	0.160	0.160	0.090	0.090
$V_\gamma^{k=2}$	0.455	0.455	0.455	0.369	0.369

COMPARISON WITH QUANTUM MONTE CARLO

In order to make sure that our LDA+ED solver with discrete bath yields reasonable results, we make a comparison with continuous-time QMC calculations [2] where the continuum bath is used. The d -orbital spectral function for t_{2g} and e_g orbitals of Co impurities in bulk Cu for $\langle n_d \rangle = 7.78$ are shown in Fig. 4 in comparison with the QMC results. In the presented LDA+ED calculations we used the bath spinorbitals from the "bath B" model and inverse temperature $\beta = 500 \text{ eV}^{-1}$. In the vicinity of E_F , that is in the region where the hybridization function was fitted, the spectral density obtained from the LDA+ED calculations corresponds well to the QMC results. The single narrow peaks visible in the QMC results below E_F are in the case of LDA+ED represented by three neighboring peaks in corresponding energy region. Similarly to the QMC results, the spectral function does not exhibit significant differences between t_{2g} and e_g types of orbitals.

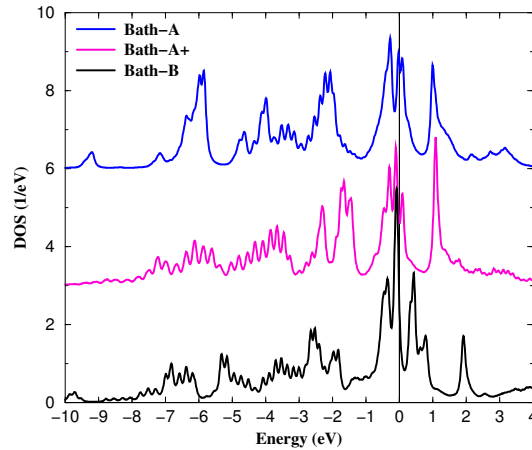


FIG. 3: (Color online) The d -orbital spectral function of Co in bulk Cu obtained from the LDA+ED calculations for three choices of the bath. Bath-A: bath with 10 spinorbitals, Bath-A+: Bath-A extended with 10 extra spinorbital parameters -2 eV below the E_F , Bath-B: bath with 20 spinorbitals in the vicinity of E_F .

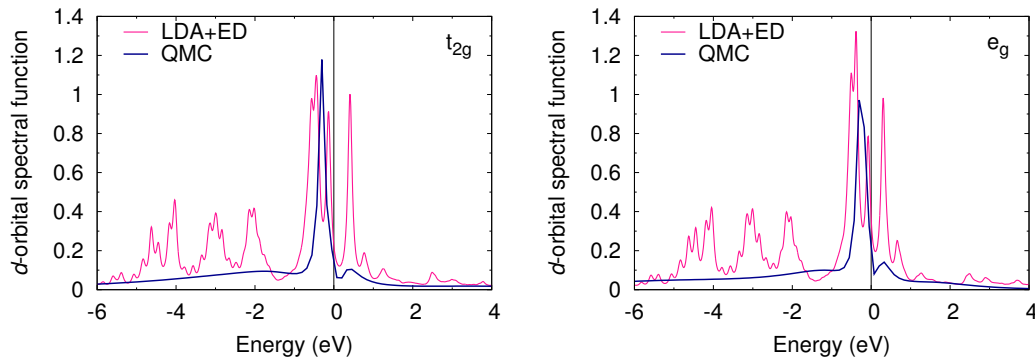


FIG. 4: (Color online) The d -orbital spectral function for t_{2g} (left) and e_g (right) orbitals of Co impurity in bulk Cu for $\langle n_d \rangle = 7.78$. Pink 'LDA+ED' - our results, blue 'QMC' results from [2].

RESULTS AND DISCUSSION

The system was analyzed for five values of the occupations of the Co d shell $\langle n_d \rangle$ ranging between 7.2 and 7.78. In all considered cases the ground state of the system is a singlet, therefore the bath of conduction electrons of the host is screening the magnetic moment on the impurity site. The two highest considered occupations $\langle n_d \rangle = 7.51$ and $\langle n_d \rangle = 7.78$ correspond to the results presented also in [2]. The values of μ corresponding to those occupations are in good agreement with those from QMC calculations and are equal approximately 26 eV and 27 eV. Due to the small value of SOC, we observe only slight differences between the results with and without it. The inclusion of the effect to the model does not change qualitatively d -orbital spectral function.

Next, we calculated the spin S , orbital L and total J moments for the considered occupations from the expectation value $\langle \hat{X}^2 \rangle = X(X+1)$, where $X = S, L$ or J , respectively. The values of the moments were decreasing with increase of the occupancy $\langle n_d \rangle$. The spin moments lay within the range 1–1.3, the orbital moments were equal approximately 3 for all occupations and the total moments were equal 3.4–3.6. Our spin moments are slightly higher than those from QMC calculations, although still in good agreement. The precise values for ED SIAM, together with those for QMC are listed in Tab. II.

Following [2] we calculated orbital-resolved quasiparticle weight Z for the orbitals t_{2g} and e_g according to the formula $Z_m = \left(1 - \frac{\text{Re} \partial \Sigma_m(\omega)}{\partial \omega} \Big|_{\omega \rightarrow 0}\right)^{-1}$.

The precise values of $Z(t_{2g})$ and $Z(e_g)$ are shown in Tab. II. For both types of orbitals Z increases with the increase of $\langle n_d \rangle$ and also exhibits good agreement with QMC results.

TABLE II: Chemical potential, occupation of the impurity d shell, spin S , orbital L and total J moments, and quasiparticle weight Z for both types of orbitals. Values obtained from our calculations and those presented in [2].

	μ (eV)	$\langle n_d \rangle$	S	L	J	$Z(t_{2g})$	$Z(e_g)$
LDA+ED	24.89	7.2	1.31	2.98	3.63	0.33	0.31
LDA+ED	25.26	7.3	1.26	2.98	3.61	0.36	0.34
LDA+ED	25.61	7.4	1.21	2.98	3.57	0.38	0.36
LDA+ED	26	7.51	1.16	2.97	3.53	0.4	0.38
LDA+ED	26.97	7.78	1.03	2.91	3.4	0.44	0.43
QMC [2]	26	7.51	1.02	–	–	0.38	0.39
QMC [2]	27	7.78	0.92	–	–	0.42	0.47

CONCLUSIONS

In this work we presented the electronic and magnetic structure for Co impurity in bulk Cu calculated with the use of LDA+ED method. In our method, we solved the multi-orbital SIAM with included SOC and effect of the cubic crystal field on the Co impurity. The model was parametrized matching to the LDA electronic structure. Among the tested ways of parametrization of the bath, the most accurate choice is the bath with 20 spinorbitals whose parameters

were extracted from the hybridization function in the vicinity of the Fermi level. The impurity model was then solved using the Lanczos method.

The calculations show that the magnetic moment of the Co impurity is screened by the conduction bands of the host and as a result the ground state of the system is a nonmagnetic singlet for all analyzed average occupations of the impurity d shell. Calculated Co d -orbital spectral functions, spin moments and orbitally resolved quasiparticle weights are consistent with the QMC results [2].

Acknowledgments

The support from the GACR grant No. 15-071725 is acknowledged.

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